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Enhanced hydrothermal conversion of surfactant-modified diatom microshells into barium titanate replicas

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The three-dimensional nanostructured SiO_2-based microshells of diatoms have been converted into nanocrystalline $BaTiO_3$ via a series of shape-preserving reactions. The microshells, obtained as diatomaceous earth, were first exposed to a surfactant-induced dissolution/reprecipitation process [C.E. Fowler, et al., *Chem. Phys. Lett.* **398,** 414 (2004)] to enhance the microshell surface area, without altering the microshell shape. The SiO_2 microshells were then converted into anatase TiO_2 replicas via reaction with TiF_4 gas and then humid oxygen. Hydrothermal reaction with a barium hydroxide-bearing solution then yielded three-dimensional nanocrystalline microshell replicas composed of $BaTiO_3$. The enhanced surface area of the surfactant-treated microshells resulted in faster conversion into phase-pure $BaTiO_3$ at 100 °C.

The attractive electronic, optical, and chemical properties exhibited by barium titanate-based compositions have led to the use of these ceramics as capacitors, thermistors, actuators, sensors, phosphors, and other devices.[1–8] A variety of approaches (e.g., mixed oxide, mixed salt, sol-gel, polymeric precursor, hydrothermal, microemulsion, mechanochemical, and combustion syntheses) have been used to synthesize $BaTiO_3$ powders with fine particle and crystal sizes.[9–19] Nanocrystalline barium titanate-based ceramics have exhibited relatively high room-temperature dielectric constants that are temperature- and voltage-stable for integrated capacitors,[20,21] high sensitivity to water vapor and carbon dioxide for gas sensors,[22–24] and enhanced response of fluorescence to temperature changes for real-time temperature monitoring.[25] The worldwide interest in nanoscale ferroelectric devices has also led to the recent syntheses of $BaTiO_3$ nanowires,[26] nanorods,[27] nanoshell tubes,[28] and nanoshell spheres.[29,30] However, the scalable fabrication of complex three-dimensional (3D) $BaTiO_3$-based nanostructures in a variety of well-controlled morphologies via synthetic methods has been a significant challenge.

Nature, on the other hand, provides impressive examples of 3D microscale to nanoscale mineral assembly.[31–39] For example, coccolithophorids (*Haptophyta*) and diatoms (*Bacillariophyta*) are single-celled algae that assemble intricate nanostructured calcium carbonate and silica microshells, respectively.[35–40] A particularly wide variety of morphologies can be found among the microshells of the estimated 10^5 species of diatoms.[40,41] Each species of diatom assembles an amorphous silica-based microshell with a particular 3D shape and a specific pattern of nanoscale features (e.g., nanoscale pores, channels, ridges, tubules).[38–40] The sustained reproduction of a given diatom species can yield enormous numbers of diatom cells with the same 3D microshell shape.[42,43] Such intricate, genetically precise, and massively parallel 3D self-assembly under ambient conditions has no analog in man-made processing. Continued progress in the genetic modification of diatoms promises to yield microshells with shapes tailored for specific applications (i.e., genetically-engineered micro/nanodevices).[44–47] However, the natural silica-based chemistry of diatom microshells limits the range of such potential applications.

Silica-based diatom microshells can be converted into

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replicas composed of other non-silica-bearing oxides through the use of gas/silica displacement reactions (i.e., via the patented Bioclastic and Shape-preserving Inorganic Conversion or BaSIC process).[48–53] For example, the following net metathetic reaction was first proposed for replacing the silica in diatom microshells with titania[49]:

$$TiF_4(g) + SiO_2(s) \rightarrow TiO_2(s) + SiF_4(g) \quad . \qquad (1)$$

Subsequent work by Unocic et al.[51] demonstrated that an intermediate reaction product, $TiOF_2(s)$, forms in advance of titania by the following reaction:

$$2TiF_4(g) + SiO_2(s) \rightarrow 2TiOF_2(s) + SiF_4(g) \quad . \qquad (2)$$

With proper control of the TiF_4:SiO_2 reactant ratio and temperature, these authors generated $TiOF_2$-based structures that retained the 3D shapes and fine features of the starting silica microshells.[51] The conversion of $TiOF_2$ into TiO_2 can then be conducted by reactions of the following type[51,54–56]:

$$TiOF_2(s) + 1/2O_2(g) \rightarrow TiO_2(s) + F_2(g) \quad , \qquad (3a)$$

$$TiOF_2(s) + H_2O(g) \rightarrow TiO_2(s) + 2HF(g) \quad . \qquad (3b)$$

Unfortunately, the standard Gibbs free energy of formation of solid $TiOF_2$, $\Delta G^o_f[TiOF_2(s)]$, at $\leqslant$350 °C is not available in common thermodynamic tables (nor apparently in the literature) to allow for thermodynamic calculation of the critical $(O_2)^{1/2}$:F_2 and H_2O:$(HF)^2$ ratios required to enable reactions (3a) and (3b) to proceed spontaneously to the right (note: although Dudley, et al.[57] recently suggested that reaction (3a) was thermodynamically unfavored, the value of $\Delta G^o_f[TiOF_2(s)]$, or a source of such data, was not provided to allow for calculation of the critical $(O_2)^{1/2}$:F_2 ratio). Nonetheless, both reactions have been successfully conducted at modest temperatures (i.e., $\leqslant$350 °C) with flowing oxygen or moist air.[51,54–56]

Coating-based approaches may also be used to alter the chemistries of diatom microshells.[58–66] If the coating is thin, continuous, conformal, rigid, and chemically robust, then silica-free structures (e.g., zirconia or polymer[60,64]) possessing the external shape of the starting microshell can be produced upon selective dissolution of the underlying silica microshell (note: if the internal and external surfaces of the microshell are coated, then dissolution of the silica will yield a hollow wall structure). Weatherspoon, et al. synthesized the first freestanding barium titanate-based microshell structures by using a sol-gel process to generate a conformal and continuous $BaTiO_3$ coating at 700 °C on chemically compatible magnesia-converted microshell replicas (formed through reaction with magnesium gas[48–50,52]).[56,62,65] Selective dissolution of the underlying magnesia then yielded freestanding phase-pure $BaTiO_3$ structures that retained the 3D microshell shape.[56]

In this paper, a combination of gas/solid and liquid/solid reactions is examined for the low-temperature syntheses of $BaTiO_3$ replicas of diatom microshells. With this approach, silica-based microshells are first converted into titania replicas via reactions (2–3b) above (as per Unocic et al.[51]) and then converted into barium titanate replicas via hydrothermal reaction with barium hydroxide-bearing aqueous solutions, as indicated below:

$$TiO_2(s) + \{Ba(OH)_2\} \rightarrow BaTiO_3(s) + H_2O(1) \quad , \qquad (4)$$

where $\{Ba(OH)_2\}$ refers to barium hydroxide dissolved within water. Such reactions allow for the synthesis of barium titanate replicas at lower reaction temperatures than for sol-gel-based approaches and could yield solid wall replicas of the microshells (as opposed to hollow wall structures that are produced with coating-based methods, upon removal of the silica). The partial hydrothermal conversion of titania microshell replicas into barium titanate was initially examined by Gaddis[66] and has since been reported by Cai et al.[56] Dudley et al.[57] have recently also reported the partial conversion of TiO_2 microshell replicas (synthesized by the method of Unocic et al.[51,56]) into $BaTiO_3$ via reaction of liquid $Ba(OH)_2{\cdot}8H_2O$ at 120 °C for 10 h. The purpose of this paper is to evaluate the use of a surfactant-based dissolution/reprecipitation process to significantly enhance the exposed surface areas of silica diatom microshells and thereby reduce the time required for complete hydrothermal conversion into barium titanate replicas.

The starting diatom microshells [obtained as flame-polished diatomaceous earth (DE) from a commercial vendor] used in the present work possessed hollow cylindrical shapes and were decorated with rows of fine (several hundred nanometers in diameter) pores [Fig. 1(a)]. Nitrogen adsorption analysis [Brunauer–Emmett–Teller (BET), Autosorb-1, Quantachrome, Boynton Beach, FL] of such DE yielded a modest surface area of 1.6 m^2/g. To significantly enhance the surface area, the silica microshells were exposed to a surfactant-induced dissolution/reprecipitation treatment similar to that reported by Fowler, et al.[67] A basic aqueous solution of hexadecyltrimethylammonium bromide (CTAB; $CH_3(CH_2)_{15}N(Br)(CH_3)_3$, Alfa Aesar, Ward Hill, MA) was prepared by dissolving 3.05 g of CTAB in 30 ml of 0.7 M NaOH. A 5.0 g batch of DE was added to this solution (i.e., a 10:1 SiO_2:CTAB molar ratio). After stirring for 15 min, the slurry was sealed in a 50 ml stainless steel container. The container was then heated to 112 °C for 72 h. After filtering and thorough washing with

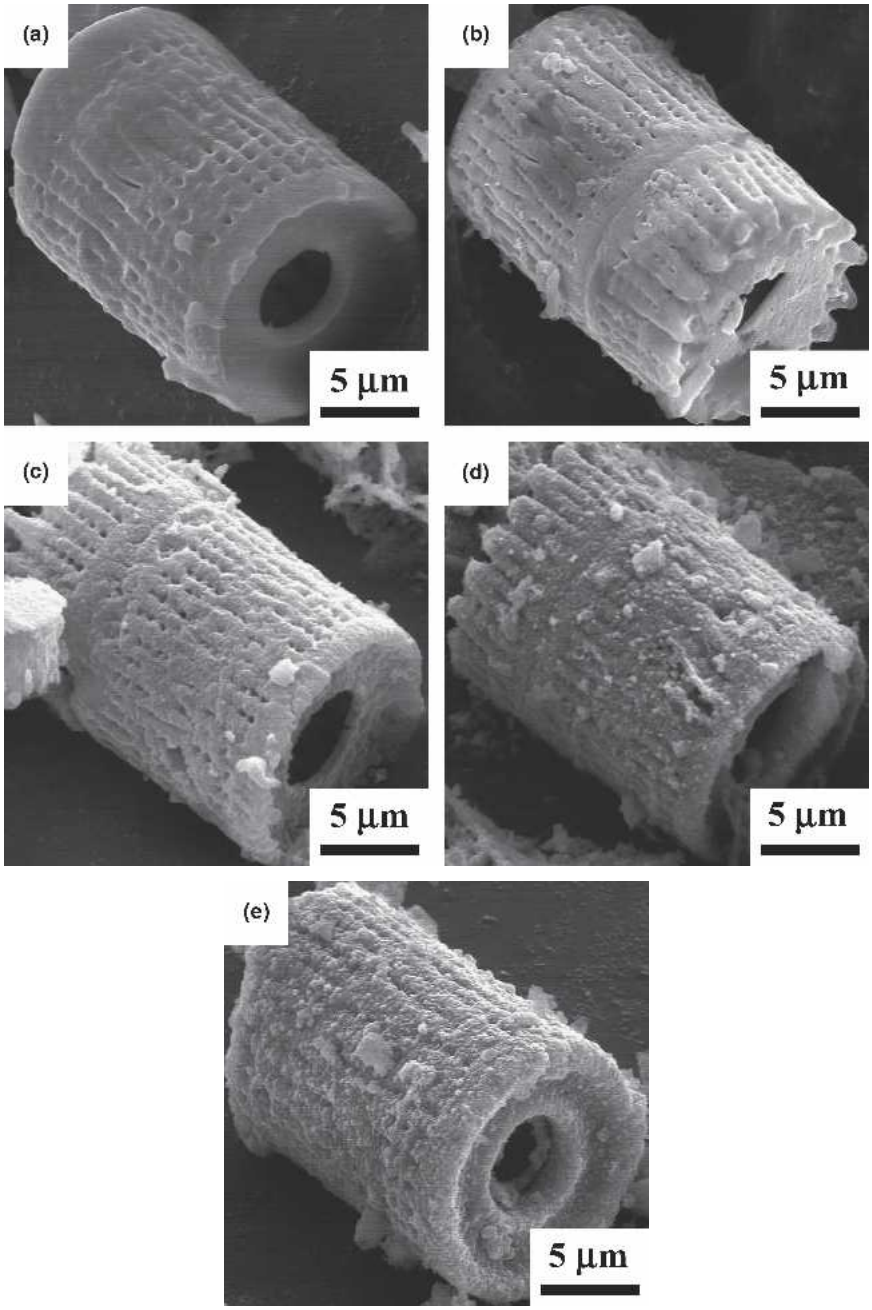

FIG. 1. Secondary electron images of: (a) a starting SiO_2 diatom microshell, (b) a CTAB-treated SiO_2 diatom microshell, (c) a CTAB-treated microshell after reactive conversion into TiO_2, (d) a CTAB-treated, TiO_2-converted microshell after hydrothermal conversion into $BaTiO_3$, and (e) a TiO_2-converted microshell (with no prior CTAB treatment) after partial hydrothermal conversion into $BaTiO_3$.

deionized water, the microshells were heated in air at 1 °C/min to 540 °C and held for 10 min (for drying and pyrolysis of residual organic material). A secondary electron image of a CTAB-treated microshell is shown in Fig. 1(b). The microscale 3D microshell morphology and surface features did not appear to be altered by this treatment. However, BET analysis indicated that the DE surface area increased by a factor of 75 to a value of 120 m^2/g.

The CTAB-treated and untreated diatom microshells were then converted into titania using the method of Unocic et al.[51,56] The SiO_2 microshells and TiF_4 [titanium(IV) fluoride, Alfa Aesar] were placed in a titanium tube (2.5 cm diameter, 17 cm long, Grade 2, McMaster-Carr, Atlanta, GA) within an argon atmosphere glove box, and the tube was welded shut. The molar TiF_4:SiO_2 ratio sealed within the tube was 2.4:1. The sealed tubes were then heated at 5 °C/min to 350 °C and held at that temperature for 2 h. After removal from the tubes, the reacted specimens were exposed to humid,

flowing oxygen (generated by passing oxygen through a water bath heated to 30 °C) for 5 h at 400 °C. X-ray diffraction (XRD) analyses indicated that this treatment resulted in complete conversion of the silica microshells into the anatase polymorph of titania. A secondary electron image of a titania/CTAB microshell is shown in Fig. 1(c) (a similar microscale morphology was observed for the non-CTAB-treated, titania-converted specimens). The cylindrical 3D morphology of the starting microshells was preserved in the titania replicas.

BET analyses indicated that the titania microshell replicas generated from non-CTAB-treated and CTAB-treated silica microshells possessed specific surface areas of 5.2 and 11.3 m^2/g, respectively. The specific surface area of the titania replicas synthesized from CTAB-treated silica was significantly lower than that for the CTAB-treated silica (11.3 versus 120 m^2/g). This decrease is likely to have resulted from the loss of fine pores (<4 nm) present in the CTAB-treated silica upon conversion into titania. Indeed, Barrett-Joyner-Halenda (BJH) analysis[68] of the nitrogen desorption curves indicated that the CTAB-treated silica possessed a significant amount of mesoporosity; that is, pores ≤4 nm in diameter comprised 68% of the cumulative volume occupied by all pores ≤50 nm in diameter. However, BJH analysis of the titania replicas generated from the CTAB-treated silica indicated that pores ≤4 nm in diameter comprised only 8.7% of the cumulative volume occupied by all pores ≤50 nm in diameter.

For hydrothermal conversion into barium titanate, 0.050 g of titania microshell replicas, 0.60 g of barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8(H_2O)$, >98% purity, Alfa Aesar), and 0.60 ml of deionized water (i.e., a molar $Ba(OH)_2 \cdot 8(H_2O)$:TiO_2:H_2O ratio of 3.0:1:53) were placed in a tube machined from a polytetrafluoroethylene rod (12.5 mm internal dia., 21.0 mm internal length, Virgin Electrical Grade PTFE, McMaster-Carr, Pasadena, CA). Such charged tubes were sealed with PTFE plugs within an argon atmosphere glove box. The sealed tubes were thrust into an oven preheated to 100 °C and held at this temperature for times up to 48 h. Upon cooling and filtration, the reacted microshells were washed 8 times with deionized water heated to 75 °C to remove residual barium hydroxide adhering to the specimen. The reacted microshells were then placed in an ultrasonic cleaner (Model 2510, Branson, Danbury, CT) for 1 h to dislodge any remaining barium hydroxide adhering to the specimens. After ultrasonication, the reacted microshells were again washed 8 times with heated deionized water. The microshells were then dried at 75 °C for 24 h.

XRD analyses obtained after hydrothermal reaction of the non-CTAB-treated and CTAB-treated titania replicas for various times at 100 °C are shown in Figs. 2(a) and 2(b), respectively. After 8 h of reaction, both types of specimens consisted of appreciable amounts of $BaTiO_3$ and TiO_2 (anatase). A substantial reduction in the amount of residual TiO_2 occurred between 8 and 24 h of reaction. The ratios of the areas of the most intense (110) $BaTiO_3$ and (101) TiO_2 diffraction peaks for the two types of specimens and for different reaction times are shown in Table I. After 8 and 24 h of reaction, the $BaTiO_3$:TiO_2

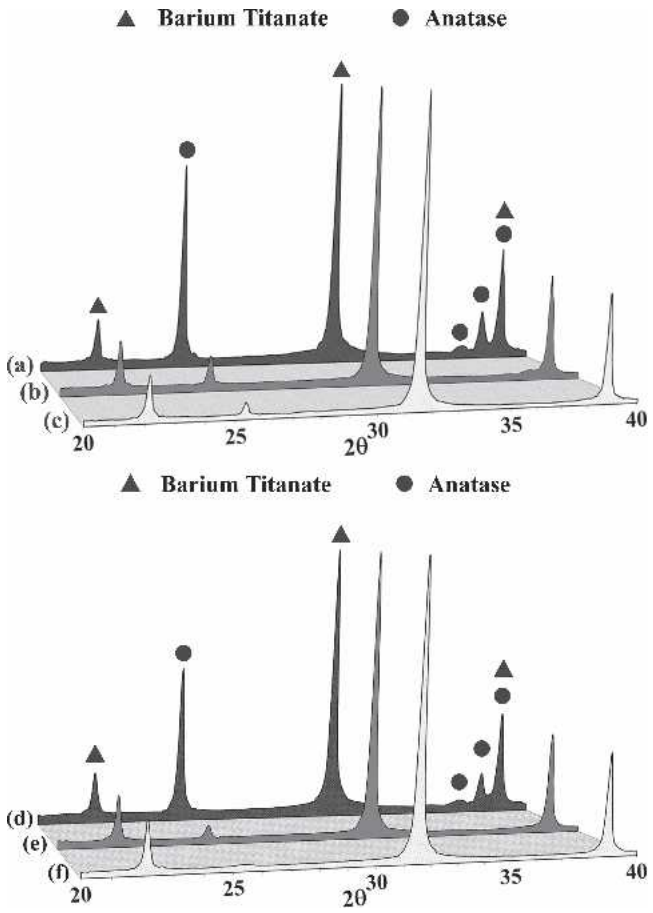

FIG. 2. XRD patterns obtained from microshell specimens after various hydrothermal reaction times at 100 °C: (a) 8 h, (b) 24 h, and (c) 48 h; and surface modified CTAB diatoms at (d) 8 h, (e) 24 h, (f) 48 h.

TABLE I. Hydrothermal conversion of TiO_2 into $BaTiO_3$ as a function of reaction time at 100 °C.

Specimen type[a]	Reaction time (h)	(110) $BaTiO_3$:(101) TiO_2[b]
DE	8	2.18
DE	24	13.4
DE	48	36.6
CTAB	8	2.61
CTAB	24	28.9
CTAB	48	…[c]

[a]DE refers to the starting microshells obtained as diatomaceous earth; CTAB refers to DE microshell specimens that were exposed to a hexadecyltrimethylammonium bromide (CTAB) surfactant-based dissolution/reprecipitation process[67] prior to reactive conversion into anatase titania.
[b]Ratio of the areas of the most intense XRD peaks for $BaTiO_3$ [the (110) peak] and TiO_2 [the (101) peak].
[c]Complete conversion into $BaTiO_3$.

peak area ratio was higher for the CTAB-treated specimens than for the non-CTAB-treated specimens. After 48 h of reaction, a detectable diffraction peak for TiO_2 (i.e., the (101) diffraction peak located near 25.3 degrees) was observed in the non-CTAB-treated specimen, whereas this peak was absent in the CTAB-treated specimen. The absence of distinct (200)-type and (002)-type peaks in the barium titanate diffraction pattern in Fig. 2(f) indicated that the $BaTiO_3$ had formed predominantly as a cubic polymorph (note: the hydrothermal formation of cubic $BaTiO_3$ at $\leqslant$150 °C has been reported by a number of authors[15,16,30,69]). Scherrer analyses of the diffraction peaks in Fig. 2(f) yielded an average crystallite size of 63 nm for the fully converted (CTAB-treated) $BaTiO_3$ microshells.

Secondary electron images of a fully converted (48 h, 100 °C, CTAB-treated) $BaTiO_3$ microshell and a partially converted (48 h, 100 °C, non-CTAB-treated) $BaTiO_3$ microshells are shown in Figs. 1(d) and 1(e), respectively. The overall 3D morphology of the starting microshells was preserved in the $BaTiO_3$-converted microshells. BET analysis of the completely converted $BaTiO_3$ specimens yielded a specific surface area of 12.8 m^2/g, which was comparable to that for the titania replicas (11.3 m^2/g) from which such $BaTiO_3$ was derived.

The hydrothermal conversion of titania templates (e.g., microspheres, nanotubes) into barium titanate structures that retained the template shape has been reported by several authors.[15,70–72] Such shape preservation is consistent with so-called "in situ" hydrothermal conversion, during which a conformal $BaTiO_3$ product layer is generated around the reacting TiO_2 template.[15,69,70,73] Hertl reported that such in situ hydrothermal conversion of titania particles at 70–103 °C was limited by the rate of reaction at the $TiO_2/BaTiO_3$ interface, when the barium hydroxide concentration in the aqueous solution exceeded 1 M (as was the case in the present work).[73] The rate of hydrothermal conversion into $BaTiO_3$ via such an interfacial reaction-limited process should certainly have been enhanced with an increase in the starting surface area of the TiO_2 replicas, as was accomplished by starting with CTAB-treated silica microshell templates.

In conclusion, silica diatom microshells have been completely converted into nanocrystalline barium titanate structures, with retention of the starting 3D microshell morphology, through the use of a series of low-temperature fluid/solid reactions. Exposure of the microshells (obtained as DE) to a CTAB-bearing aqueous solution at 112 °C resulted in a significant enhancement in the microshell surface area without an appreciable change in the 3D microscale morphology. Subsequent reaction of the microshells with titanium tetrafluoride at 350 °C for 2 h, and then with humid oxygen at 400 °C for 5 h, yielded titania (anatase) microshell replicas. Hydrothermal reaction of the titania replicas with a barium hydroxide solution at 100 °C for 48 h resulted in complete conversion into nanocrystalline barium titanate structures that retained the 3D microscale microshell morphology. The enhanced surface area of the CTAB-treated microshells resulted in an increase in the specific surface area of the TiO_2 microshell replicas that, in turn, led in an increase in the rate of hydrothermal conversion into $BaTiO_3$ at 100 °C.

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